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# ToF-SIMS analysis of adsorbate/membrane interactions

## I. Adsorption of dehydroabiatic acid on poly(vinylidene fluoride)

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### Abstract

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was used to investigate the adsorption behaviour of aqueous solutions of dehydroabiatic acid (dhAA) in contact with poly(vinylidene fluoride) (PVdF). An identification scheme was developed to qualitatively identify the presence of adsorbed resin acid on the membrane surface at solution concentrations from 10–1000 ppm. ToF-SIMS reveals that dehydroabiatic acid adsorbs inhomogeneously on the surface of poly(vinylidene fluoride).

### 1. Introduction

In recent years, increasingly stringent emission guidelines have prompted the pulp and paper industry to examine new available technologies to treat effluent pollution. Specialised polymeric materials, such as ultrafiltration and nanofiltration membranes, have been effectively used to selectively separate undesirable organic pollutants [1–3]. Much of the research work being carried out in this area deals with the macroscopic properties of these materials, such as flux decline [4–6].

Major advances in commercial surface analytical equipment over the last twenty years have prompted many researchers to look beyond the traditional ‘bulk’ methods of evaluating membrane properties, and to reevaluate the role that surface morphology

and surface chemistry play in the fouling behaviour of membranes. Information related to specific solute/membrane interactions is essential for maximising the separation efficiency in present systems, and to aid in the development of membrane technology. The use of surface spectroscopic techniques to study polymer/adsorbate interactions offers a number of advantages over the more traditional analytical methods: examination of the outer atomic layers of the membrane, which must influence the adsorption properties of the material; microscopic examination of individual adsorption sites; and identification of fouling behaviour at very low (parts per million (ppm)) adsorbate concentrations which are inaccessible to conventional techniques.

Static Secondary Ion Mass Spectrometry (SSIMS) is an attractive choice for such studies because it offers extreme surface sensitivity (sub-monolayer), very low detection limits (ppm or ppb) and, when combined with the time-of-flight capability, permits very high mass resolution to differentiate similar

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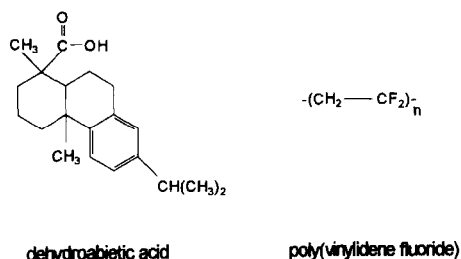


Fig. 1. Chemical structures of dehydroabietic acid and PVdF.

mass fragments. Despite these obvious advantages, there has been little work published on the use of static SIMS in adsorption/fouling studies [7–13].

This paper details the use of a model system to examine the interaction of organic pollutants found in pulp and paper effluent with membranes presently used for their removal. The choice of membranes and foulants, and the range of foulant concentrations were all chosen to reflect typical conditions which are found in industrial use. The model system chosen for examination involves a single representative pollutant, dehydroabietic acid, interacting with poly(vinylidene fluoride). Feeder samples taken from pulp and paper mills in Thunder Bay [14] and Fort William [15] showed dehydroabietic acid to be present in the range of 39 to 78 ppm, and that dhAA is the major constituent of the resin and fatty acids. Dehydroabietic acid (dhAA) is a resin acid (MW 340.28) which has the chemical formula  $C_{20}H_{28}O_2$ , while poly(vinylidene fluoride), or PVdF, is a fluorinated polymer. The structures of the two materials are shown in Fig. 1.

This paper reports on the application of Time-of-Flight SIMS to membrane fouling, by examining the adsorption behaviour of poly(vinylidene fluoride) in contact with aqueous solutions of dehydroabietic acid in the concentration range 0–1000 ppm. The detection limits for this pollutant/membrane system are determined by ToF-SIMS.

## 2. Experimental

### 2.1. Time-of-flight secondary ion mass spectrometry (ToF-SIMS)

The SIMS analyses were carried out on a Kratos Prism ToF-SIMS instrument with a reflectron mass analyzer which is capable of mass resolution,  $m/\Delta m$ ,

> 5000 at  $m/z$  27. The base pressure of the instrument was  $\sim 5 \times 10^{-8}$  Pa ( $4 \times 10^{-10}$  Torr). The instrument uses a 25 keV  $^{69}\text{Ga}$  liquid metal ion source (LMIS) and was run at a working pressure of  $\sim 5 \times 10^{-7}$  Pa ( $4 \times 10^{-9}$  Torr). The total ion flux was kept below  $10^{13}$  ions/cm<sup>2</sup> per experiment, which is within the static regime [16]. A rastered ion beam produced an analysis area of 200  $\mu\text{m}^2$  (i.e.  $14.1 \mu\text{m} \times 14.1 \mu\text{m}$ ). A minimum of 3 areas were analysed per sample unless otherwise stated. The negative ion spectra of both the membrane and the dehydroabietic acid were run, but the ion intensities were extremely low and did not yield any useful information. Therefore, only the positive ion spectra were used. Mass calibration of low resolution spectra was achieved using ion peaks from  $\text{H}^+$ ,  $\text{C}^+$ ,  $\text{CH}^+$ ,  $\text{CH}_2^+$ ,  $\text{CH}_3^+$ ,  $\text{C}_2\text{H}_2^+$  (occasionally),  $\text{C}_2\text{H}_3^+$  (occasionally), as well as  $\text{Na}^+$ , and  $\text{Mg}^+$  when present. High mass resolution spectra were calibrated using the aforementioned peaks (except  $\text{CH}_2^+$ ), as well as implanted  $\text{Ga}^+$ , and additional peaks whose identity could be unambiguously determined. Charge neutralisation of the non-conducting surfaces was achieved using a low energy electron flood gun. The instrument was used in the pulsed-mode, wherein the ion beam was pulsed in sequence with the flood gun and the detector using 100–150 ns pulse widths. An analyzer (collection) resolution of 10 ns was used for the low resolution spectra, and either 625 ps or 312 ps resolution was used for the high resolution spectra. The data was transferred (for deconvolution) at 10 ns or 1.25 ns resolution, respectively, for the low and high resolution spectra. The high mass resolution spectra are presented using the following format: The twenty (or twenty-five) most abundant ion fragments above  $m/z$  15 (excluding inorganic impurities) are tabulated in decreasing order of intensity. Each mass fragment, designated by its mass-to-charge ratio ( $m/z$ ), is presented with its assigned chemical identity. In cases where the identity of an ion peak cannot be unambiguously assigned to an individual species, the additional chemical identities are included. If an individual ion mass contains two (or more) chemical species which are not completely resolved in the mass spectrum (i.e.  $m/z$  69 =  $\text{CF}_3^+$  on PVdF and  $= \text{C}_5\text{H}_9^+$  on dehydroabietic acid), then the contribution of each chemical species to the total ion intensity is estimated.

## 2.2. Sample / solution preparation

Polymer samples were cut into  $\sim 1 \text{ cm}^2$  coupons and placed into a Soxhlet extraction apparatus, where the membranes were alternately refluxed in reagent grade hexanes, methanol, and distilled water. The membranes were air dried (5–15 min) prior to insertion into the spectrometer vacuum system.

Solution preparation was as follows: Dehydroabietic acid (Pfaltz and Bauer, Inc.; technical grade) was crushed to a fine powder using a mortar and pestle. Distilled water was used to make up all of the solutions. The distilled water was filtered through a glass frit funnel prior to use. A quantity of reagent grade ethanol was used to solubilise the resin acid. Usually, about 10% of the total solution volume was made up of ethanol. Solutions were made up in volumetric flasks and refrigerated when not in use. After sitting refrigerated for two weeks, any unused solution was discarded and fresh solutions were prepared. In most cases, freshly prepared solutions were used for each new experiment. Approximately 100 ml of test solution was poured into a 150 ml beaker and set vigorously stirring. Membrane samples were left in the stirred solution for 24 h at room temperature. The beakers were covered with a watch glass to prevent contamination or evaporation of the solutions during testing. The membranes were removed from the test solutions and rinsed in an ultrasonic bath for  $2 \times 0.5 \text{ h}$  with two 80 ml portions of distilled water. After air drying ( $\sim 5 \text{ min}$ ), the samples were placed into the spectrometer for SIMS analysis.

The polymer used in this study was a commercially prepared sample of poly(vinylidene fluoride) (PVdF), prepared from a Koch membrane (HFM 180).

## 3. Results and discussion

### 3.1. Reference spectra

#### 3.1.1. Poly(vinylidene fluoride)

A sample of the high resolution SIMS spectra of PVdF is presented in Fig. 2. As expected, fluorinated species dominate the ion fragments. Low resolution spectra were recorded from six areas (not shown).

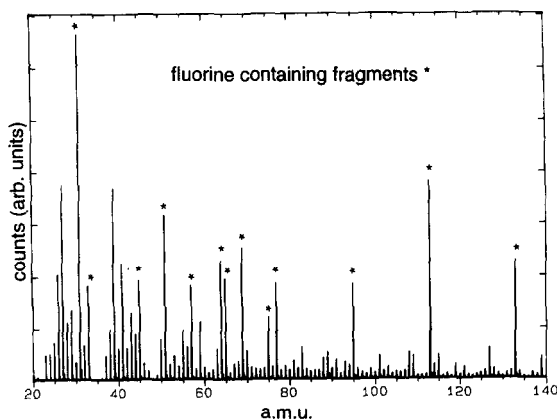


Fig. 2. ToF-SIMS spectrum of PVdF.

The analyses yielded fairly consistent spectra with varying amounts of  $\text{Na}^+$  and  $\text{Ca}^+$  as impurities.

#### 3.1.2. Dehydroabietic acid

An example of the low resolution ToF-SIMS spectra obtained from dehydroabietic acid (pressed on graphite tape) is displayed in Fig. 3. Since dehydroabietic acid is a partially saturated/partially unsaturated organic acid, its fragmentation pattern will reflect these qualities. As can be seen from the tabulated data, there are very few oxygenated species. This is unfortunate, because oxygenated fragments would provide distinctive 'signatures' that would aid in identification of the adsorbed acid on the membrane surface. The importance of this point will become apparent when dealing with very weak concentrations of resin acid.

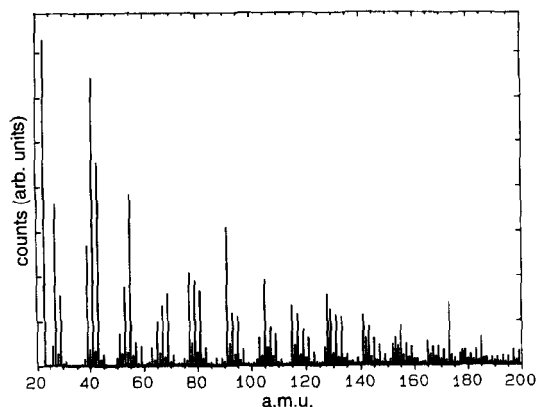


Fig. 3. Low resolution ToF-SIMS spectrum of dehydroabietic acid.

### 3.2. Identification scheme

An identification scheme was developed to determine the presence of dehydroabietic acid adsorbed on the surface of the poly(vinylidene fluoride). Using the twenty or twenty-five most intense ion peaks obtained from the high resolution SIMS analysis of dehydroabietic acid and poly(vinylidene fluoride), and choosing only ion fragments whose identity was unambiguously assigned, a 'signature' of ion peaks for each material can be observed under low resolution SIMS conditions. Ion fragments which are common to both the membrane, PVdF, and dehydroabietic acid (including the low mass ( $\leq 43$  amu) hydrocarbon fragments), are excluded from this identification scheme. The signature peaks can be used to qualitatively identify the presence of both PVdF and dhAA.

The signature peaks chosen for PVdF include the following mass fragments (Table 1):

The signature peaks chosen for dhAA include the following mass fragments (Table 2):

### 3.3. Adsorption experiments

The adsorption experiments were carried out as outlined in the Experimental Section. A series of dehydroabietic acid solutions were prepared with the

Table 2

Signature peaks for dehydroabietic acid

$m/z$	Identity
53	$C_4H_3^+$
55	$C_4H_7^+$
67	$C_5H_7^+$
79	$C_6H_7^+$
91	$C_7H_7^+$
105	$C_8H_9^+$
115	$C_9H_7^+/C_6H_{11}O_2^+$

Note: there are several peaks between  $m/z$  115–175 which may be useful for identification.

following concentrations: 1000 ppm, 250 ppm, 100 ppm, 50 ppm, 10 ppm, and 1 ppm. The following section presents the ToF-SIMS results carried out on membranes tested in each of the solutions in succession, and a discussion of each set of results.

#### 3.3.1. PVdF + 1000 ppm dehydroabietic acid solution + 1 h rinse

A series of PVdF membranes were immersed in 1000 ppm dehydroabietic acid solutions and then rinsed in an ultrasonic bath for one hour. Following the adsorption experiments, the membranes were analysed for the presence of adsorbed dehydroabietic acid. A summary of the high resolution ToF-SIMS results are presented in Table 3.

At a solution concentration of 1000 ppm, detection of dehydroabietic acid on PVdF is fairly straightforward using the 'signature' peaks previously assigned to each material. The series of low resolution ToF-SIMS spectra displayed in Fig. 4 illustrates the presence of ion peaks due to both dehydroabietic acid and poly(vinylidene fluoride). The spectra also show an inhomogeneous distribution of resin acid on the membrane as evident by the varying intensities of the two sets of ion peaks.

It is worthwhile to comment on the distribution of adsorbed dehydroabietic acid on the PVdF membrane. The fact that the ToF-SIMS results show the presence of both resin acid and PVdF on all areas analysed indicates that the resin acid is inhomogeneously adsorbed on the surface of the PVdF, although the thickness of the adsorbed layer is not known. This statement should be qualified. It is *possible* that some of the resin acid has desorbed from the membrane as a result of the rinsing proce-

Table 1

Signature peaks for poly(vinylidene fluoride)

$m/z$	Identity
31	$CF^+$
32	$CHF^+$
33	$CH_2F^+$
38	$C_3H_2^+$
45	$C_2H_2F^+$
51	$CHF_2^+$
59	$C_3H_4F^+$
64	$C_2H_2F_2^+$
65	$C_2H_3F_2^+$
74 <sup>a</sup>	$C_3F_2^+$
75	$C_3HF_2^+$
95	$C_3H_3F_3^+$
108 <sup>a</sup>	$C_4H_3F_3^+$
113	$C_3HF_4^+$
133	$C_3H_2F_5^+$

<sup>a</sup> Peaks not among the 20 most intense, but useful for identification.

dure, but we are unable to measure any desorption using ToF-SIMS. The rinsing water was not analysed for traces of dehydroabiatic acid, although some solid material has been observed. On the basis of the adsorption experiments, one can definitively state that desorption, if present, is partially or wholly irreversible under the rinsing conditions used in this study.

However, all of the results have been examined under the premise that the polymer surface is completely flat. This assumption is not completely true. First, the polymer chains which comprise the membrane surface contain fine structure, which appear as 'nodules' in a secondary electron image (see Fig. 5) [17]. These nodules can be seen to have a diameter of approximately  $\frac{1}{4} - \frac{1}{2} \mu\text{m}$ , hence an estimate of the surface roughness can be obtained as one-half the nodule diameter. This corresponds to  $\sim 125\text{--}250$  nm. Beyond this range, there may be gross changes in the surface roughness which cannot be estimated. The membrane also contains pores of a finite size and distribution. Both of these factors will influence the measured signals in ToF-SIMS. Fig. 5 shows secondary electron micrographs taken of a PVdF membrane (HFM180 Koch) at two different magnifi-

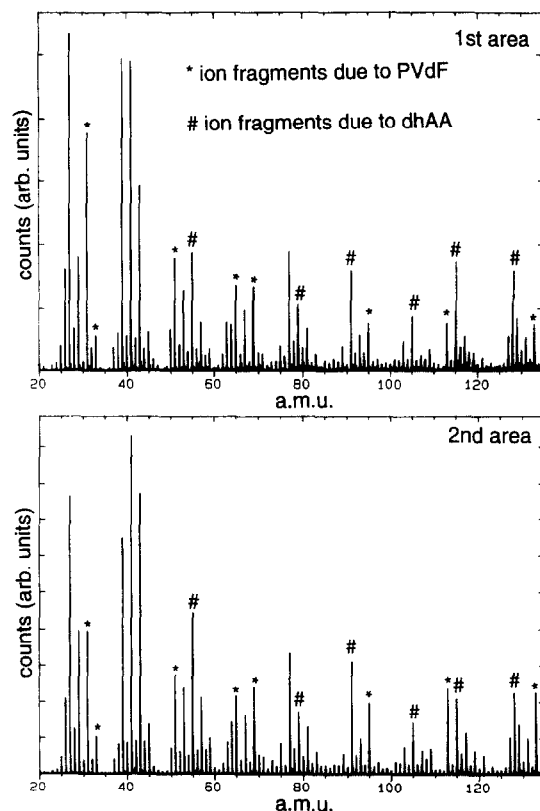


Fig. 4. ToF-SIMS spectra of PVdF immersed in 1000 ppm dhAA solution + 1 h rinse.

Table 3

ToF-SIMS analysis of PVdF+1000 ppm dhAA solution + 1 h rinse

Ranking	$m/z$	Identity
1	27	$\text{C}_2\text{H}_3^+$
2	41	$\text{C}_3\text{H}_5^+$
3	39	$\text{C}_3\text{H}_3^+$
4	31	$\text{CF}^+$
5	29	$\text{C}_2\text{H}_5^+$
6	43	$\text{C}_3\text{H}_7^+$
7	26	$\text{C}_2\text{H}_2^+$
8	55	$\text{C}_4\text{H}_7^+$
9	51	$\text{C}_4\text{H}_3^+/\text{CHF}_2^+$
10	77	$\text{C}_6\text{H}_5^+$ and $\text{C}_3\text{H}_3\text{F}_2^+$
11	53	$\text{C}_4\text{H}_5^+$
12	91	$\text{C}_7\text{H}_7^+$
13	113	$\text{C}_3\text{HF}_4^+$
14	65	$\text{C}_5\text{H}_5^+/\text{C}_2\text{H}_3\text{F}_2^+$
15	45	$\text{C}_2\text{H}_2\text{F}^+$
16	115	$\text{C}_9\text{H}_7^+/\text{C}_5\text{H}_7\text{O}_3^+$
17	128	$\text{C}_{10}\text{H}_8^+$
18	64	$\text{C}_2\text{H}_2\text{F}_2^+$
19	57	$\text{C}_4\text{H}_9^+$
20	33	$\text{CH}_2\text{F}^+$

cations. One set of micrographs shows a pristine membrane, while the second set shows a membrane fouled by a mill feed. The membranes were fouled by permeation tests, not through simple static adsorption tests as was the mechanism involved in this work. The outline from the fouled membrane has a 'string-like' structure on its surface. Large empty spaces are visible just below the top surface of the membrane. These spaces, called 'voids', form during the casting process.

### 3.3.2. PVdF + 250 ppm dehydroabiatic acid solution + 1 h rinse

Eight areas of the immersed PVdF membrane were analysed by low resolution SIMS. All eight areas show ion peaks due to *both* dhAA and PVdF, although the relative concentrations of both species vary among the regions. This suggests an inhomogeneous distribution of resin acid on the PVdF. The

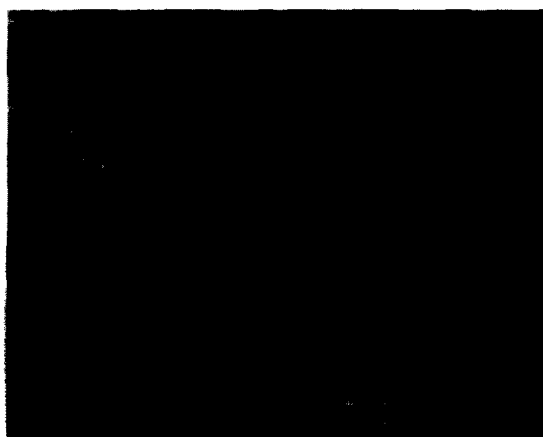
presence of dhAA and PVdF was determined from the 'fingerprint' mass fragments previously detailed (see 1000 ppm case for details). Two high resolution analyses were also run to verify the peak assignments.

### 3.3.3. PVdF + 100 ppm dehydroabietic acid solution + 1 h rinse

The 'fingerprint' ion fragments used previously with the 1000 ppm and 250 ppm treated membranes were inadequate to determine the presence of resin acid adsorption at 100 ppm concentrations on the low resolution spectra. The five regions analysed by high resolution ToF-SIMS displayed some minor differences among the spectra, but none of the varia-

tions were believed to be significant. The low resolution analyses (five regions) yielded fairly consistent spectra, but offered no clues as to the presence of adsorbed resin acid. The low concentrations of resin acid used in these tests made identification of adsorbed dehydroabietic acid very difficult, and rendered the 'signature peaks' unreliable for positive identification. Therefore, a more intensive screening process was developed to determine the presence of adsorbed dehydroabietic acid at solution concentrations less than 250 ppm. This scheme uses high resolution analysis of individual peaks to elucidate the presence of any resin acid. The following peaks were chosen as potentially suitable for identifying adsorbed dehydroabietic acid on PVdF (Table 4).

a) Clean PVdF Membrane



b) Fouled PVdF Membrane

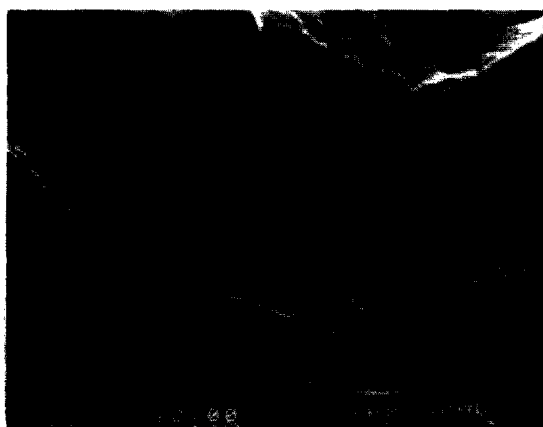
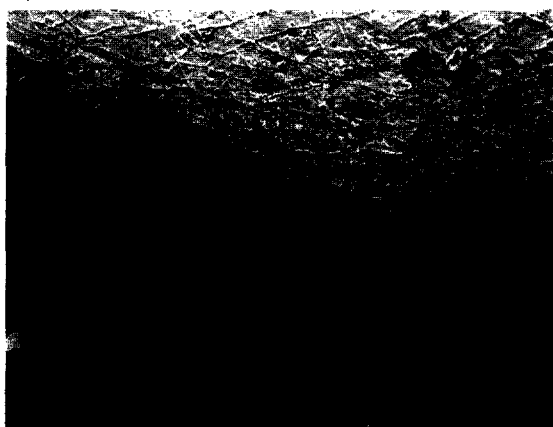


Fig. 5. Secondary electron micrographs of pristine and fouled PVdF membranes.

Table 4  
Ion masses used for resin acid identification

Ranking <sup>a</sup>	$m/z$	dhAA	PVdF
11	69	$C_5H_9^+$	$CF_3^+$ ( $C_5H_9^+$ (small shoulder))
8	77 <sup>b</sup>	$C_6H_5^+$	$C_3H_3F_2^+$
6	91	$C_7H_7^+$	nothing
12	105	$C_8H_9^+$	nothing

<sup>a</sup> Determined from high resolution spectra of dehydroabietic acid.

<sup>b</sup> Exact masses of the two ions are very similar: i.e.  $C_6H_5^+ = 77.0391$  and  $C_3H_3F_2^+ = 77.02026$ .

Despite the perceived suitability of the  $m/z$  77 ion peak as a reliable identification tool, it was found to consistently yield a negative result when used as part of the identification scheme at solution concentrations  $\leq 100$  ppm.

Two additional peaks were selected for identification purposes.  $m/z$  115  $C_3H_3F_4^+$  (exact mass 115.01706), has a weak intensity in the PVdF spectra, and is a complementary peak to the intense peak at  $m/z$  113,  $C_3HF_4^+$ . Dehydroabietic acid also contains a peak at mass 115; namely,  $C_9H_7^+$  (exact mass 115.0574). High resolution SIMS can differentiate between the masses of these two peaks, enabling identification of the two ion species. High resolution SIMS performed on nine samples confirmed that untreated (i.e. clean) PVdF membranes contain *only*  $C_3H_3F_4^+$ . The presence of both  $C_3H_3F_4^+$  and  $C_9H_7^+$  ions would indicate dehydroabietic acid adsorption on PVdF. The second peak chosen for identification was  $m/z$  141. Dehydroabietic acid contains a weak ion peak,  $C_{11}H_9^+$ , at this mass. Confirmation of this peak was taken as a spectral intensity of  $\geq 2 \times$  background intensity. Nine samples of PVdF were analysed by high resolution SIMS to verify that no ion peak exists at mass 141 on the untreated membrane. Since the spectral intensity of all the identification peaks will be very weak, confirmation of adsorbed dehydroabietic acid will be determined on the basis of the overall profile obtained from the identification scheme, rather than from the results of any one or two individual ion peak(s).

The results of this new scheme as applied to the 100 ppm adsorption experiments are presented in Table 5. The convention to be used in Table 5 and subsequent tables is that 'yes' indicates confirmation of the identification peak, while 'no' indicates its absence. The identification summary suggests that

Table 5  
Identification of dehydroabietic acid (from 100 ppm solution) on PVdF

ID peaks	Yes	No	Maybe
$m/z$ 69	(1)(2)(4)(5)	(3)	
$m/z$ 77		(1)(2)(3)(4)	(5)
$m/z$ 91	(1)(2)(3)(4)(5)		
$m/z$ 105	(1)(2)(3)(4)(5)		
$m/z$ 115	(1)(2)(3)(4)(5)		
$m/z$ 141	(1)(2)(3)(4)(5)		

Identifications summary: Area (1), 5 yes and 1 no; Area (2), 5 yes and 1 no; Area (3), 4 yes and 2 no; Area (4), 5 yes and 1 no; Area (5), 5 yes and 1 maybe.

dehydroabietic acid is present in all five areas of the membrane examined by ToF-SIMS.

### 3.3.4. PVdF + 50 ppm dehydroabietic acid solution + 1 h rinse

The results obtained from low resolution ToF-SIMS analysis taken on five regions of PVdF exposed to 50 ppm dehydroabietic acid solution indicate that the spectra are highly consistent, although some relative variations exist. Of the six areas that were analysed by high resolution SIMS, only very minor differences were noted among the spectra. The detailed identification scheme was used to identify resin acid residues on the membrane surfaces (Table 6). The identification summary suggests that regions (1)(2)(5) likely contain adsorbed dehydroabietic acid, while regions (3)(4) show no resin acid present. The results for region (6) are inconclusive.

Table 6  
Identification of dehydroabietic acid (from 50 ppm solution) on PVdF

ID peaks	Yes	No	Maybe
$m/z$ 69		(3)(4)	(1)(2)(5)(6)
$m/z$ 77		(1)(2)(3)(4)(5)(6)	
$m/z$ 91	(1)(2)(5)	(4)(6)	(3)
$m/z$ 105	(1)(2)(5)	(3)(4)(6)	
$m/z$ 115	(1)(2)(5)	(3)(4)	(6) <sup>a</sup>
$m/z$ 141	(1)(2)(5)	(3)(4)	(6) <sup>a</sup>

<sup>a</sup> Very low intensity in area (6), making the assignment questionable.

Identification summary: Area (1), 4 yes, 1 no and 1 maybe; Area (2), 4 yes, 1 no and 1 maybe; Area (3), 5 no and 1 maybe; Area (4), 6 no; Area (5), 4 yes, 1 no and 1 maybe; Area (6), 3 no and 3 maybe.



Table 7

Identification of dehydroabietic acid (from 10 ppm solution) on PVdF

ID peaks	Yes	No	Maybe
$m/z$ 69	(2)(4)	(3)(5)(6)	(1)
$m/z$ 77	(6)	(2)(3)	(1)(4)(5)
$m/z$ 91	(2)(3)(5)(6)		(1)(4)
$m/z$ 105	(2)(4)	(1)(3)(5)	(6)
$m/z$ 115	(4)(5)(6)	(2)	(1)(3)
$m/z$ 141	(6)	(1)(2)(3)(5)	(4) <sup>a</sup>

<sup>a</sup> Borderline intensity, i.e.  $\sim 2 \times$  background.

Identification summary: Area (1), 4 maybe and 2 no; Area (2), 3 yes and 3 no; Area (3), 1 yes, 4 no and 1 maybe; Area (4), 3 yes and 3 maybe; Area (5), 2 yes, 3 no and 1 maybe; Area (6), 4 yes, 1 no and 1 maybe.

### 3.3.5. PVdF + 10 ppm dehydroabietic acid solution + 1 h rinse

Although a large number of regions were analysed by low resolution ToF-SIMS (eleven regions on two different samples), the variations among the spectra were quite subtle and made it impossible to determine whether any dehydroabietic acid was adsorbed to the surface. Many of the 'characteristic (or fingerprint) peaks' previously used to qualitatively determine the presence of adsorbed fatty acid on the membrane surface were no longer reliable indicators. At 10 ppm concentration of the resin acid, even minor peaks from the membrane which were previously ignored must now be considered for their potential interference. The detailed analysis of the six regions recorded from high resolution SIMS is presented below (Table 7). The summary results suggest that area (6) may contain dehydroabietic acid, while area (4) is questionable. There is not enough evidence to support the existence of resin acid in any of the other areas analysed.

### 3.3.6. PVdF + 1 ppm dehydroabietic acid solution + 1 h rinse

Three areas were analysed by low resolution SIMS, and two areas by high resolution SIMS. The low resolution spectra were quite consistent, although there were some relative peak variations among the three areas. The high resolution ToF-SIMS results showed some minor differences between the spectra of the two regions, but none of the variations were believed to be significant. Most of the charac-

teristic peaks used for resin acid identification fell within the background noise of the SIMS spectra. As a further verification, a series of blank runs were completed on PVdF membranes. The testing procedure for the blank runs was identical to the method used for the samples involving the resin acid, except that the solutions contained no dehydroabietic acid. The slight variations noted among the spectra treated with 1 ppm resin acid solutions were within the level of noise noted among the blank runs. It is felt that the test procedure involving 'signature peaks' is inconclusive for samples immersed in solutions with less than 10 ppm content of dehydroabietic acid. Therefore, on the basis of these spectra alone, it is not possible to confirm the presence of any adsorbed resin acid on the PVdF. The use of a distinctive chemical marker attached to the resin acid, such as an isotope, or an inorganic element (i.e. Cl) would provide a conclusive SIMS 'signature' which may enable the determination of very low resin acid concentrations i.e.  $< 10$  ppm.

No specific information is currently available about the nature of the dehydroabietic acid in solution. Dehydroabietic acid has amphipathic properties, containing both polar and non-polar groups. This property causes dehydroabietic acid to form micelles in solution. The size and shape of these micelles at different concentrations is not known. This uncertainty compounds the difficulty in detecting the adsorbed resin acid on the membrane, especially at very low solution concentrations. If the dehydroabietic acid is adsorbed on the membrane surface as micelles, then the vigorous cleaning procedure in the ultrasonic bath may 'break' the micelles into smaller aggregates (cohesive failure), thereby removing some of the material from the surface. However, the basic layer at the membrane/dhAA interface would be unaffected due to the strong adhesive forces.

The ToF-SIMS results show that adsorptive fouling behaviour of PVdF occurs at very low dhAA solution concentrations. Adsorption of any material on a membrane will have a deleterious effect on its performance—the size ratio between the foulant and pores is the essential factor involved. Possible fouling mechanisms are shown below in Fig. 6 [18]. In case (a), adsorption occurs only on the surface because the pores are too small to allow dhAA to enter. At the opposite extreme, the foulant is very small

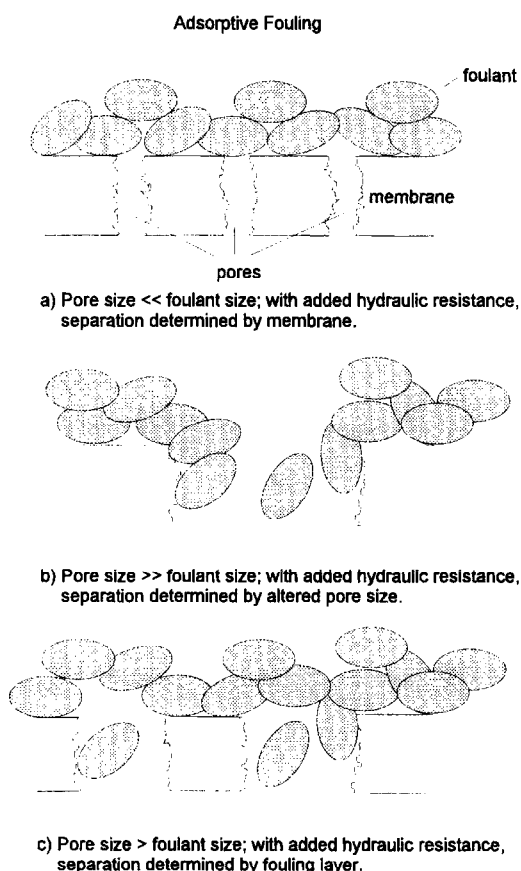


Fig. 6. Schematic diagram illustrating the principles of adsorptive fouling.

compared to the pore size, case (b). An intermediate case, (c), is observed when adsorption occurs both in the pores and on the surface. In each case, the hydraulic resistance is increased resulting in lower fluxes. The retention capability of the membrane is also changed. In case (a), retention is still determined by the membrane. Case (b), described as the pore restriction model, results in a smaller effective pore size. The form in which dhAA exists in solution, either as unimolecular and/or micellar structure(s), will have a profound influence on which adsorption mechanism applies. The molecular weight cut-off of the PVdF is rated at 100 kDaltons, while the molecular weight of dhAA is only 300 g/mol. In this case, unimolecular dhAA can adsorb both on the surface and within the pore itself (case (b)). Considering micellar dhAA, both the size of the micelles and

the likelihood that the micelle structures will remain intact after adsorption will determine the adsorption mechanism. It is, therefore, possible that multiple fouling mechanisms are occurring.

With a SIMS sampling depth of  $\sim 1$  monolayer, only the top surface of the membrane or adsorbed material is examined. The sampling area is  $\sim 14 \times 14 \mu\text{m}$ , which would include  $10^2$ – $10^4$  pores; hence, information gained from ToF-SIMS represents an average of clean PVdF and adsorbed dhAA, found both on the pores and on the surface. Therefore, the specific fouling mechanism cannot be identified at the present time.

#### 4. Conclusions

This exploratory study describes the application of ToF-SIMS to the complex problem of membrane fouling. This study has yielded some insight into the interactions between dehydroabiatic acid and poly(vinylidene fluoride), and the usefulness of ToF-SIMS to study these interactions. The information gained through this study is important on two levels. First, it provides some fundamental results on the interaction of a 'model', small molecule/one membrane system. On an applied level, this study has yielded adsorption data from a commercial membrane and known foulant, dehydroabiatic acid, using solution concentrations which reflect industrial conditions.

ToF-SIMS has confirmed the presence of adsorbed dehydroabiatic acid on PVdF membranes from solution concentrations ranging from 10 ppm to 1000 ppm. The detection limit of ToF-SIMS in this adsorbate/membrane system is the 10 ppm dhAA solution. Using the present detection scheme, this lower limit appears to be governed by the intrinsic properties of the resin acid/membrane system rather than instrumental limitations. The detection of lower concentrations may be possible through isotopic substitution.

The ToF-SIMS analyses indicate that the resin acid is adsorbed inhomogeneously on the surface of the membrane. This suggests that specific adsorption sites may be present. This phenomenon is likely influenced by the presence of micelles.

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